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HYGROTHERMAL EFFECTS IN CONTINUOUS FIBRE REINFORCED COMPOSITES

PART II: PHYSICAL PROPERTIES

J. P. Komorowski

National Aeronautical Establishment

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**HYGROTHERMAL EFFECTS IN CONTINUOUS FIBRE
REINFORCED COMPOSITES**

PART II: PHYSICAL PROPERTIES

**EFFETS HYGROTHERMIQUES DANS LES COMPOSITES
À RENFORT DE FIBRE CONTINU**

PARTIE II: PROPRIÉTÉS PHYSIQUES

by/par

J.P. Komorowski

National Aeronautical Establishment

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OTTAWA
SEPTEMBER 1983

AERONAUTICAL NOTE
NAE-AN-10
NRC NO. 22700

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SUMMARY

— This report is second in a series of literature reviews in which hygrothermal effects on aerospace composite materials (CM) with polymeric matrixes are examined. This report (Part II) deals primarily with the glass transition temperature and expansion properties due to temperature and moisture. The chapter on residual stresses is also included in this part as these stresses are a direct consequence of the expansion properties. Specific heat, thermal conductivity and emittance are briefly mentioned in Chapter 3.0, while properties connected with moisture absorption have been reviewed extensively in Part I of the series.

Other reports in this series deal with the following topics:

- Part I: Thermal and Moisture Diffusion
- Part III: Mechanical Properties 1
- Part IV: Mechanical Properties 2
- Part V: Composite Structures and Joints
- Part VI: Numerical and Analytical Solutions
- Part VII: Summary of Conclusions and Recommendations

A complete list of references is included in the Appendix and the numbers in the brackets appearing in the text refer to this list.

RÉSUMÉ

Le présent rapport est le deuxième d'une série de dépouillements bibliographiques concernant l'influence des effets hygrothermiques sur les matériaux composites utilisés en aérospatiale. Cette Partie II porte principalement sur la température de transformation vitreuse et la dilatation sous l'effet de la chaleur et de l'humidité. Le chapitre sur les contraintes résiduelles figure dans cette partie puisqu'elles résultent directement de la dilatation. La chaleur spécifique, la conductibilité thermique et le pouvoir émissif sont traités brièvement au chapitre 3.0, tandis que les propriétés découlant de l'absorption d'humidité avaient fait l'objet d'un examen détaillé dans la Partie I de la série.

Les autres rapports de la série portent sur les sujets suivants:

- Partie I: Diffusion de la chaleur et de l'humidité
- Partie III: Propriétés mécaniques 1
- Partie IV: Propriétés mécaniques 2
- Partie V: Structures et joints composites
- Partie VI: Solution numériques et analytiques
- Partie VII: Résumé des conclusions et recommandations

Une liste complète des références est incluse en annexe et les nombres entre parenthèses dans le texte se rapportent à cette liste.

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HYGROTHERMAL EFFECTS IN CONTINUOUS FIBRE REINFORCED COMPOSITES

PART II: PHYSICAL PROPERTIES

1.0 INTRODUCTION

The second part of the series of literature reviews* is concentrated on three properties: the glass transition temperature and expansions due to temperature and moisture. The properties connected with moisture absorption were dealt with extensively in Part I of the review.

Specific heat, thermal conductivity and emittance have not received very much attention from researchers in composites and therefore are only mentioned briefly.

Other properties may be affected by the absorption of moisture or heat but are considered of secondary importance or trivial (i.e. effect on specific weight) and are not therefore addressed in detail.

Material properties responsible for ultrasonic wave propagation were found to be affected by moisture and hygrothermal degradation. Those interested in Non Destructive Testing (NDT) of composites are referred to Kaelble and Dynes^[153, 155, 95, 152], Ishai and Bar-Cohen^[138, 139] and Kriz^[180].

The changes in electrical properties may also be useful for NDT purposes as was shown by Cotinaud et al^[68], Dewimille^[87] (see Part I of review) and Kadotani^[151].

The Appendix is a revised version of the bibliography for the whole series of reviews on Hygrothermal Effects on aerospace composites.

2.0 GLASS TRANSITION TEMPERATURE

At room temperature most polymer matrix materials are in a glassy state. On increasing the temperature, the elastic moduli and viscosity decrease slowly until a point is reached at which both these quantities drop drastically within a temperature range of 2° to 5°C. Discontinuity in the change of properties does not take place, however, the rates of change of various physical properties versus temperature undergo large increases. Similar effects were observed for crystals and denoted as second order transitions. However, in polymers the derivative properties do not appear to be discontinuous as in the case of crystals and to stress this difference, the use of the term glass transition temperature (T_g) is preferable to second order transition temperature^[215].

The transition from a glassy to rubbery state is observed as a drastic drop in the mechanical properties of the matrix materials and is a natural upper temperature limit for structural applications of these materials. Glass transition temperature (T_g) is therefore one of the important composite material properties.

2.1 Methods of Measurements

Glass transition is manifested when a rapid rate of change of various physical and mechanical properties is observed with a slight increase in temperature. As a consequence, many methods have been used to measure the T_g. The methods can be either static or dynamic.

* Only polymer matrix continuous fibre reinforced composites are considered (see Introduction to Part I).

Torsional braid analysis (TBA) is a commonly used dynamic method (Fig. 1) (ASTM2236-81). The frequency and the rate of decay of free vibrations of a pendulum are monitored with changing temperature. Transition temperature is recorded as a significant change in complex elastic shear modulus or more precisely as a maximum in the logarithmic decrement.

Static methods are more popular and generally easier. They include dilatometry, columnar loading (or linear thermal expansion method), differential thermal analysis and other methods. In dilatometry, the coefficient of cubical thermal expansion is monitored. A rather abrupt change in the value of the coefficient over a narrow temperature interval indicates the glass transition temperature.

The T_g values vary from test method to test method as the concept of second order transition is not precise. For this reason other tests were designed (i.e. Heat Distortion Temperature tests (HDT), Vicat softening temperature using a penetration probe) and are used to establish temperature envelope of polymers and for qualitative comparisons. What separates them from methods used for T_g measurement is that they do not measure any fundamental physical property. Data obtained from those tests is especially useful in applications where the factors of time, temperature, method of loading, and fiber stress are similar to those specified in that test [ASTM D648-72(78)].

Very popular tests, the heat distortion temperature (HDT) tests can have several forms (see ASTM D648-72(78) and ASTM D1637-61(76)). The HDT test, usually in the form of three point flexural displacement under constant loading, is an empirical method and does not measure any fundamental property. The temperature designated as HDT is arbitrarily chosen and therefore should not be referred to as glass transition temperature but simply as HDT. HDT tests may be useful in qualitative comparison of materials.

Tajima^[283] compared results obtained using two different test methods. Materials tested were 5209 epoxy and T300/5209 composites. For dry resin, the HDT was 139°C while T_g from dilatometry was 154°C. Sykes et al^[281] used TBA (Fig. 1) and HDT (Fig. 2) for the same T300/5209 composite. The difference between T_g from TBA and HDT was very pronounced for wet composites (Fig. 3).

Carter et al^[52] suggested a practical method of defining a T_g value from a heat distortion experiment (flexural). Their method is demonstrated in Figure 4 and based on an equation derived from a viscoelastic model of cross-linked polymer. The curves shown represent probe displacement (δ) vs temperature (T). The point of maximum curvature (T_c, δ_c) is found by visual inspection or numerical analysis. The intersection between a line parallel to temperature axis at the distance of $3.60 \delta_c$ and a tangent to the curve at (T_c, δ_c) gives T_g . This T_g value was in good agreement with results obtained from loaded columnar expansion (where a change in the first derivative of expansion curve is used as T_g). Carter et al designate the temperature of which this second order transition takes place as T_2 rather than T_g .

It should be mentioned here that the loads used in measuring the T_g or HDT usually have to be optimized for each material to increase sensitivity. The results of HDT or T_g measurement tests are generally repeatable to better than 2°C. Reproducibility is somewhat lower, but for worst conditions, should not exceed 10°C (ASTM D1637-61(76), D3418-82, D2236-81).

2.2 Glass Transition Temperature in Composites and Neat Resins

Browning et al^[41] measured HDT of neat 3501-5 resin and AS/3501-5 composite. They do not make a distinction between HDT and T_g and refer to the measured softening point in deflection of their sample as T_g . The value of HDT for the dry resin was 177°C as opposed to 189°C for the composite. However, Tajima and Wanamaker^[283] worked with 5209 resin and T300/5209 composite. For these materials, the result of HDT and T_g (dilatometry) tests were opposite to Browning's. Both the HDT and T_g of neat resin was higher than those for the composite in the dry state. These seemed to indicate that the effective cross-link density in the matrix is less than that in the neat resin. In the wet state the situation was reversed and the T_g and HDT values of wet composite were higher than those of wet resin (see Table 1).

2.3 Effect of Moisture on Glass Transition Temperature

The effect of moisture on Tg and HDT of epoxies and their composites has been studied extensively [8, 281, 41, 42, 211, 214, 220]. Typical results are shown in Figure 5. Even a small moisture content will lower the Tg of these materials considerably. Carter and Kibler [51] measured the effect of moisture on glass transition temperature for F178 polyimide resin. From Figure 6, it can be seen that the effect is similar to that observed in epoxies.

The lowering of Tg and HDT by moisture is observed regardless of the method of measurement. However, as McKague [214] pointed out, the column loading method is better suited for wet Tg measurement as the extension of the specimens core is measured. The surface is dried during the experiment and shrinks which must have an effect on bending tests.

Browning et al [41, 42] used Equation (1) suggested by Kelley and Bueche [165] to predict Tg of wet resin.

$$T_g = \frac{\alpha_p V_p T_{gp} + \alpha_d (1 - V_p) T_{gd}}{\alpha_p V_p + \alpha_d (1 - V_p)} \quad (1)$$

where:

- α — expansion coefficient
- V — volume fraction
- suf_p — denotes polymer
- suf_d — denotes diluent

This equation is based on free volume theory. Browning used $\alpha = \alpha_i - \alpha_e$ where α_i and α_e are the linear expansion coefficients above and below Tg respectively. Browning et al had to assume the Tg of water as 4°C. Their results correlated well with measurements of Tg (or rather HDT) for 3501-5 resin (Fig. 7).

Delasi and Whiteside [81] modified Equation (1) by using specific volume of water values calculated from swelling measurements. This modification gave good correlation, especially for neat resins.

McKague [211, 214] observed that measured Tg temperatures from loaded column measurements are lower than those predicted by Equation (1). He pointed out that good correlation was obtained only for bending tests where drying of specimen surface affects the results. His modified equation introduces α_p as a volumetric expansion coefficient of a polymer in the glassy state. Swelling is also accounted for in his modified equation. The two models are compared in Figure 8.

Morgan and Mones [220] simplified Kelley and Bueche's equation. Since the expansion coefficient α_d 'amorphous water', was not known, it was assumed to be equal to α_p . The Tg of water was taken between 137°K and 182°K and the results compared with experimentally determined Tg for TGDDM-DDS epoxy-moisture system (see Fig. 9). The large discrepancy in results was attributed to the fact that in free volume theory, the hydrogen bonding interactions of active sites within epoxy are not accounted for. Morgan and Mones suggested that the Kelley-Bueche equation should not be used for predicting wet Tg in epoxies.

Carter and Kibler [51] proposed an entropy model for predicting glass transition temperatures in wet resins and composites. This model designates configurational entropy, rather than free volume, as the temperature dependent function that determines this transition. Arbitrary assignments for Tg and α of water are avoided and hydrogen bonding is accounted for. After some simplifying assumptions, the following Equation (2) is obtained:

$$T_{gf} = T_{g0} \{1 - (R/M_i \Delta C_p) y(r)\} \quad (2)$$

where:

$$y(r) \equiv r \ln \frac{1}{r} + (1 - r) \ln \frac{1}{1 - r}$$

$$r \equiv (M_s/M_w) f$$

$Tg_f(^{\circ}K)$	—	glass transition temperature of material containing f grams of water per gram of dry resin
$Tg_o(^{\circ}K)$	—	Tg of dry resin
$M_s(\text{g/mole})$	—	effective formula weight of hydrogen bond site
$\Delta C_p(\text{cal/g}^{\circ}C)$	—	jump in specific heat due to glass transition in dry resin
R	—	universal gas constant
$M_w = 18 \text{ g/mole}$	—	formula weight of water

Carter and Kibler encountered difficulties in measuring ΔC_p so a final comparison of the two models was not possible at the time. For some materials, when parameters in Equation (1) are well chosen, equally good correlation with experimental values may be obtained with both models. However, as shown in Figure 6, for some resins Equation (2) gives much better correlation. The full potential of this model will be realized when problems with ΔC_p measurement are overcome.

When studying the relationships of Tg, peak thermal spike and moisture, McKague^[211] pointed out the importance of moisture distribution. In Figure 10, the two different moisture distributions shown result in the same allover moisture content. However, wet Tg may be locally exceeded leading to accelerated moisture absorption and deterioration of material (see Part I and Part III of the review).

2.4 Conclusions

- 1) HDT is often referred to as Tg. This should be avoided as the two temperatures may be substantially different.
- 2) Moisture significantly lowers the Tg and HDT of matrix resins^[41, 42, 81, 211, 214, 220, 281].
- 3) HDT assessments of wet materials should not be based on flexural type tests^[214].
- 4) The loaded column expansion method seems to be better suited for wet Tg measurement^[214].
- 5) A study comparing tests in which a fundamental property is being measured and from which Tg may be determined would be useful. At present it is difficult to relate results obtained in various laboratories using various methods.
- 6) Of all the models used for predicting wet Tg of composites reviewed here, the entropy model seems most promising. However, problems with some measurements, i.e. ΔC_p will have to be overcome before it becomes practical^[51].

3.0 THERMAL PROPERTIES — COEFFICIENT OF THERMAL EXPANSION

When considering thermal effects in solids, specific heat, thermal conductivity, emittance and coefficient of thermal expansion (CTE) are the most often used properties. Recently, the first three mentioned properties have not received much attention from researchers in composite materials.

The methods of measuring of these properties are fairly well established and the ASTM standards are good references in this case. However, finding published values of these properties for specific composites is not usually easy. For graphite/polyimide, notably, Campbell and Burleigh^[49] conducted an extensive study of these properties and some results are shown in Figures 11, 12 and 13. Christensen presented methods of predicting values of these properties for composite materials^[6] (Chapter IX).

The fourth of the above mentioned properties, namely the CTE, has been extensively measured by various researchers and some of their results will be discussed below. Matrix materials generally have very different CTE from the fibers. As the composites are cured at elevated temperature, there is on cooling to the normal usage temperature, a complex stress state created due to this CTE mismatch. These residual stresses may cause loss of dimensional stability or even failure of the interface or matrix material. Another reason for the interest in the CTE of composites, is that due to the negative CTE of the graphite fibers and the positive CTE of the resin matrices, laminates with practically zero CTE, within wide range of temperatures, may be made (e.g. graphite/epoxy antennae, telescopes). Hertz^[130] in Figure 14 gave good illustration of the advantage of composites for applications where stiffness, dimensional stability and weight are of primary concern.

Rogers, Yates et al published a series of articles on the linear thermal expansion of composites^[243, 324, 325, 326, 327, 242]. An interferometric (Fizeau) method was used to measure the changes of CTE within a temperature range of 90°K to 400°K (500°K). A large amount of data was produced using different graphite fibers, orientations, fiber volume fractions, resin types and lay-ups. The effects of matrix curing characteristics and fiber weave types on CTE were also investigated. Materials used in these studies included HTS and HMS graphite fibers, ERLA 4617/m PDA, DLS 351/BF₃ 400 and code 69 (Fathergill & Harvey Ltd) epoxy resins. CTE of neat resins, unidirectional and multidirectional lay-ups were measured.

The results provide useful data which can be immediately applied. When these data were compared with current predicting methods, generally good correlation were achieved. However, a major drawback to the application of these theories, is the lack of precise data on the CTE of fibers as well as their transverse elastic properties. When appropriate values are assigned to these thermoelastic constants, current techniques account well for fiber volumes (v_f) in the range of 0.5 to 0.8 at room temperature. Measurements have shown that the higher the fiber content v_f — the higher is the temperature at which resin softening effects on CTE are observed. Accuracy of predictive methods for CTE of composites was improved when detailed data on the temperature dependence of CTE of the neat resin had been used.

Experience gained from the response of simple lay-ups to temperature change has enabled the behavior of progressively more complex structures to be predicted with some degree of confidence according to Yates et al^[326].

Recently, Parker et al^[229] have expanded data on the CTE of graphite/epoxies by testing Fibredux 914C resin both neat and reinforced with HTS fibers. The scatter for this system was higher than for those previously tested by Rogers, Yates et al. The averaged results are, however, fairly representative for the graphite/epoxy systems. Some of these data are shown in Figures 15, 16 and Table 2.

Wang et al^[303] conducted a study of CTE of Modmor II graphite in an epoxy resin (unspecified). They used static and creep tests to obtain data on the mechanical properties of fibers and epoxy separately. This data was later used to calculate CTE of laminae and the results were compared with experimental data (Fig. 17). Wang et al also made comparison between direct measurement and co-ordinate transformation (Fig. 18). For a bidirectional laminate, a comparison was made between direct measurement and lamination theory (Fig. 19). All theories used were linear elastic and generally good correlation was obtained except for high temperatures where viscoelastic properties become more pronounced. The results agree well with conclusions reached by Rogers, Yates et al. Parker et al^[229] also compared theory with experiment for multidirectional laminates (Fig. 20). According to Parker, the poor correlation for 0/±45° laminates was caused by the presence of moisture in the specimens.

Cairns and Adams^[45] measured the thermal expansion for 3501-6 resin and its unidirectional composites made with AS graphite and S2 glass fibers. The data were compared with results obtained from a micromechanical analysis based on finite element methods. The correlation was poor. This was, according to Cairns and Adams, mainly caused by the fact that transverse CTE of fibers was not known (a sensitivity study of the model was undertaken, however, no synergistic effects were considered).

Kabelka^[150] formulated a model for predicting the CTE of fabric reinforced composites. Comparison between the model and experimental results (Fig. 21) show poor correlation. Kabelka concluded that this should improve when the viscoelastic response of matrix material is included. In a previously mentioned study, Rogers et al^[242] found that for fabric reinforced graphite/epoxies:

- fiber tow densities play a critical role in governing the average values of in plane CTE of laminates,
- the crimp in reinforcing fibers is a significant factor in controlling the temperature at which resin softening effects become apparent in the out of plane thermal expansion behavior,
- laminate stacking may change the thermal expansion by as much as 100%.

Camahort et al^[46] thermally cycled near zero CTE laminates. A near zero CTE lay-up was designed from results obtained on unidirectional specimens and was found to be $[0^\circ_4, \pm 40^\circ, \pm 70^\circ]$. Cycling was severe as samples were alternately immersed in liquid nitrogen and boiling water. Materials and corresponding results can be seen in Table 3. The CTE was measured over a range of temperatures from -1°C to 38°C . An increase of CTE was found to be caused by microcracking of the resin — the angle plies ceased to contribute and the laminate acted like a unidirectional one. The lower cure resin system marked 339 (121°C cure) performed better than the 177°C cure systems, as did the hybrid system where T300 plies made of woven graphite were added and these in effect acted as crack stoppers.

CTE of graphite/polyimide systems used by Campbell and Burleigh^[48] showed scatter during temperature changes. According to these authors, this was also caused by microcracking of the resin.

Tennyson^[286, 287] studied the effect of six months of temperature cycling from 24°C to 93°C in vacuum ($10^{-7} \sim 10^{-8}$ torr) on CTE. Over 30 cycles were applied during the whole test. Samples used were four ply $\pm\theta$ symmetrically balanced laminates of graphite, boron or Kevlar in an epoxy matrix. The results can be seen in Figures 22, 23 and 24. CTE predictions for laminates were calculated using unidirectional laminae properties in their respective environments. These are compared with data in Figures 25 and 26. Very good correlation was achieved. From these results Tennyson concluded that outgassing (mainly H_2O) and microcracking significantly affects CTE. Removal of moisture seems to increase CTE of $\pm\theta$ laminates (a similar observation was made by Parker^[229]).

For 3501 epoxy, moisture seemed to have just the opposite effect (Adamson^[41]). Dry epoxy samples had CTE equal to $8.0 \pm 0.5 \times 10^{-5}^\circ\text{C}^{-1}$ while a sample saturated (7.3% wt gain) at 74°C with moisture displayed CTE equal to $1.9 \pm 0.5 \times 10^{-4}^\circ\text{C}^{-1}$. (Adamson measured volumetric expansion.) Adamson described his observations of thermal expansion and swelling of epoxies in terms of free volume theory and postulated an equilibrium state existing between bound and unbound water in the resin. As free volume is inversely proportional to temperature, so is the volume of unbound water in the epoxy. As only bound water causes swelling it is important that CTE measurements for wet specimens allow for the time needed to reach equilibrium between bound and unbound water. Adamson found that one hour was sufficient time for this equilibrium to be reached at 25°C , however, at 1°C 24 hours were needed.

For applications where dimensional stability is of primary importance, two methods of sealing the composites from moisture were suggested at General Dynamics (Hartz^[130]). Both the bonded aluminium foil and tin-indium eutectic over a thin coat of copper proved to be effective barriers up to 1500 hours of exposure. However, besides affecting the weight of the composite ($\sim 0.13-0.21 \text{ g/in}^2$) the coatings affected the CTE. For unsealed GY70 - X30 [(0/45/90/-45)₂]₂ the CTE was $-0.017 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ($-15^\circ \div 24^\circ\text{C}$) and $+0.021 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ($24^\circ \div 74^\circ\text{C}$). When sealed with 0.02 mm single layer aluminium, the CTE changed to $+0.058 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $+0.089 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ respectively.

Useful data for CTE of composites at cryogenic temperatures can be found in References [163 and 65].

4.0 MOISTURE EXPANSION OF COMPOSITES

The absorption of moisture into the composite poses a problem of dimensional stability very similar to the one caused by thermal expansion. Current polymer matrices absorb moisture and expand (swell) as a result. Most fibers (glass, graphite, boron) do not seem to absorb moisture and restrict the matrix expansion especially in the longitudinal direction of unidirectional lamina. An internal stress state is thus created along with dimensional changes. Yet another stress state is created when expansion of a lamina is restricted by adjacent plies in a multidirectional laminate. Since moisture distribution through the thickness of a composite is generally not uniform, this type of internal stress may be present even in unidirectional laminate [Part I of the review].

By analogy to thermal effects, most theoretical prediction techniques developed for thermal expansion are applicable. Work by Marom and Cohn^[206] is a good example of the applicability using analogies. Schapery's theory was used there to predict coefficients of swelling of single lamina parallel and transverse to fibers (μ_L and μ_T). Swelling of unidirectional laminae (E glass/Araldite F/HT 972 or ERL 2256 epoxy) was measured in plane every 15° from 0° to 90° . The results were compared with two predictions, one based on Schapery's theory, and the other based on measured μ_L and μ_T . In Figure 27, comparison is made between the results. Schapery's equations should give better correlation if wet properties of constituent materials (resin) are used.

Menges and Gitschner^[216] also used this analogy and applied Schneiders equations. The relations obtained between swelling strains and fiber volume fraction were used to produce the graph shown as Figure 28.

In moisture expansion of polymeric composites, the most important problem is the expansion of the matrix material. Shirrel and Halpin^[262], in their review paper, compared experimental data from Hertz, Browning and McKague with the theory based on the assumption of additivity of volumes:

$$V_{\text{DRY LAMINATE}} + V_{\text{H}_2\text{O}} = \text{Swollen volume}$$

Within the restrictions that the moisture distribution is uniform and the resin material isotropic, the dilatational strain is:

$$e = \frac{1}{3} \frac{\Delta V}{V_0}$$

In Figure 29 the correlation seems to be good and differences with respect to expansion due to moisture among various epoxies are small.

However, results from more recently published experiments do not lend themselves to interpolation using assumptions based on additivity of volumes (see Figs. 30, 31 and 32). Hahn and Kim^[118] developed a micromechanics model in which the expansion of the resin takes place after the voids are filled with absorbed moisture. For each sample, there is a threshold value of moisture

concentration below which no expansion takes place. Above the threshold the expansion is linear with moisture content. Hahn and Kim assumed that material behavior is elastic and that swelling strains are independent of temperature. Experiments did not quite agree with this model as some expansion could be seen below the threshold value (C_v) in Figure 31.

Adamson^[4] used the concept of free volume to explain the thermal expansion and swelling of cured epoxy resins (see Review Part I, page 15). The free volume is the difference between the measured volume and the occupied volume. The occupied volume consists of mass volume plus the vibrational volume. In the first stage of moisture absorption only a fraction of absorbed water becomes bound to the epoxy network and causes swelling. The rest of the absorbed moisture occupies the free volume. The second stage of moisture absorption begins when the free volume is completely filled with water and all absorbed water becomes bound causing swelling. In this second stage, swelling is equal to the volume of absorbed water. In the third stage of swelling observed by Adamson water occupies free volume contained by micelles (highly cross-linked dense centers of generally less dense resin) and swelling again is less than the volume of absorbed water. As the equilibrium between bound and unbound water is inversely proportional to temperature (free volume changes with temperature, Fig. 33), swelling is also dependent on temperature. For a given amount of water in the sample, swelling will increase with an increase in temperature. With changes in temperature, it is very difficult to separate the effect of swelling from the pure thermal expansion in an experiment.

5.0 CONCLUSIONS (Chapter 3.0 and 4.0)

- 1) There is a lack of data on the transverse properties of fibers which in turn limits usefulness of theoretical predictions of CTE of composites.
- 2) Accuracy of predictive techniques for CTE of laminae are improved when the dependence on temperature of the fiber properties and even more so, the resin matrix are included in the analysis.
- 3) CTE of laminates can be predicted if physical properties of unidirectional laminae are known.
- 4) The hydrothermal history of the laminate may have an effect on its CTE, (i.e. thermal cycling which results in the microcracking of the resin matrix).
- 5) Moisture in the specimen complicates the measurement of CTE and in general, wet specimens require longer time at temperature before any change in dimension is measured. Wet composites have different CTE than the dry ones.
- 6) Even very thin layers of coating (aluminium or other metal coating which serves as moisture barrier) changes CTE of laminates significantly.
- 7) Swelling is significant in current polymeric composites. It can be predicted with the same expressions used for predicting the CTE. These predictions are improved when the wet properties of resins are used.
- 8) Resin swelling seems to be a three stage process that can be best explained with a free volume concept.

6.0 RESIDUAL STRESSES

The thermal and moisture expansion properties of fibers and matrices are such that internal stress states are present in composites under general conditions. These residual stresses may be responsible for both defects and dimensional instabilities of cured composite materials before any external load is applied.

6.1 Micromechanics

As described in previous chapters, fibers and resins have greatly varying expansion coefficients. The cure temperature of resins which are of interest here, is typically between 120°C and 180°C. Immediately after cure and before cool down, the resin is in a leathery state and any stresses created at this stage will be relaxed almost instantly. During the cool down to room temperature, the resin becomes more elastic and, owing to the mismatch of expansion coefficients and restraints provided by the fibers, an internal stress state will result. This type of stress was studied in model materials made of thick glass filaments embedded in birefringent resins (epoxies typically are birefringent materials). Recently, Cunningham et al.^[75] used this method and obtained photoelastic data using a polarizing microscope. The principal stresses were obtained with an oblique incidence method. A plot of loop stress around the fiber is shown in Figure 34. The maximum loop stresses at the surface of the fiber were calculated to be approximately 100 MPa (tensile) while radial stresses were only 6 MPa (compression).

Adams and Miller^[2, 218] conducted finite element inelastic analyses of hygrothermal microstresses and their results generally agree well with Cunningham's photoelastic investigation. The magnitude of these microstresses was sufficient to cause yielding of the matrix. Hygrothermal cycling was shown to change the state of residual microstresses with subsequent dimensional instability of laminae.

Menges and Gitschner^[216] demonstrated yet another mechanism for the rise of residual stresses in the transverse direction. In this direction, resin swelling is hardly restrained by the fibers, yet stresses still build up. Fiber distribution may be homogeneous or inhomogeneous (see Fig. 35). For both types of distributions zones of high and low fiber content may be identified and these will have different swelling strains. As a result, local residual stresses are present, and as Menges and Gitschner estimated, may lead to microcracking of the resin in a glass/resin composite.

6.2 Macromechanics

Residual stresses have been observed in composite materials not only at the microscopic level, but also at the macroscopic level in angle plied laminates or in unidirectional hybrids. These stresses have been studied experimentally and analytically by numerous authors.

Chamis^[53] provides a good review of NASA Lewis Research Center activities and of NASA sponsored research in this field. He pointed to four factors from which lamination residual stresses (LRS) originate:

- 1) the differences in the ply CTE in the longitudinal (α_{11}) and in the transverse (α_{22}) direction. $\alpha_{22}/\alpha_{11} \cong 20$ for fiber/resin laminae;
- 2) the difference in ply orientation angle (θ) — there are no LRS in unidirectional laminates;
- 3) the difference between fabrication temperature and use temperature;
- 4) the ability of a ply to support stresses along its material axes.

Water is present in laminates under general usage conditions which implies, from the results of the previous chapter and from literature which will be reviewed below, that point one above should be broadened to include the difference in moisture expansion, as well as CTE. However, general points brought forward by Chamis are still true owing to the analogy between moisture and thermal effects.

The existence of LRS is evidenced by transply cracks and warpage of unsymmetric angle-plied laminates before any mechanical load was applied to them. The transply cracks are observed when LRS exceed the ply transverse strength (typically 28-63 MPa)^[53]. Molcho and Ishai^[219] observed these cracks in a graphite/epoxy T300/5208 skin for a control surface. The original lay-up

contained 0° and $\pm 45^\circ$ plies and after curing, not only transverse but also interlaminar cracks were observed. The latter originated from the tips of transverse cracks. It is worth noting that they found a uniform distribution of plies, as opposed to a laminated lay-up, to be preferable, as it resulted in less severe cracks.

Strain gauges have been employed in LRS measurements. Daniel, Liber and Chamis^[78] embedded strain gauges during fabrication of laminates. Results for 0° plies of baron/epoxy [$0_2/\pm 45^\circ$], laminate are shown in Figure 36.

Pagano and Hahn^[228] used a simpler method of LRS measurement. They bonded gauges to laminates at RT and then heated them to cure temperature.

The most common method of measuring LRS is through deformation measurements of unsymmetric laminates. Unsymmetric laminates warp due to the existence of LRS. This method is however indirect as it is necessary to use lamination theory to obtain stress values corresponding to the measured warpage.

Chamis in his review reported on use of linear elastic laminate theory for ply thermal stresses (LRS caused by cure temperature being different than the use temperature). Effects of some material variables were analyzed with the aid of this model. In Figure 37(c) the effect of the lamination of plies in angle-ply laminate is shown and correlates well with the earlier mentioned findings of Molcho and Ishai. The effect of fiber volume ply angle, and matrix modulus is shown in Figures 37(a), (b) and 38.

Lee, Lewis and Sacher^[188, 189] used [$90^\circ/0^\circ/90^\circ$] glass/epoxy systems to study the effect of moisture on their mechanical properties. First ply failure, in the tension test, results in a change in slope of the stress-strain curve. Lee et al called this the yield point. They observed that yield strain was affected by residual strain (Fig. 39) and these in turn changed with the amount of moisture in the composite. They measured residual stresses in symmetric laminate by the deply technique. When one of the plies was removed, the laminate warped and the stresses could be calculated.

Pagano and Hahn^[228], Hahn^[119] and Hahn and Kim^[118] developed a linear elastic model to analyze curing stresses, however, they used a temperature dependent elastic moduli. Measurements of warpage in unsymmetric angle ply laminates were compared with predictions. The stress free temperature (T_0) was observed to be below the curing temperature. For T300/5208 and Scotchply 1002 (glass/epoxy) it was 121°C as opposed to a cure temperature of 177°C . In transverse direction it was found that the curing stresses may be more than 50% of UTS in this direction. For swelling, a moisture threshold model was used and it was found that moisture absorption may result in a stress free laminate at room temperature (Fig. 40). Correlation of experimental data with calculated values was not always satisfactory.

The elastic model does not account for significant stress relaxation, especially near the T_g of the resin. The lowering of the stress free temperature in a composite due to annealing, can readily be explained on the basis of a viscoelastic model. Crossman, Warren and Pinoli^[73] studied the relations between residual stresses and annealing time and temperature (see Fig. 41). For Shell 1031 resin (190°C cure) the residual stresses at room temperature were lowered by 25% or $\sim 7\text{ MPa}$ after 16 hours at 121°C . Moisture, it was concluded, by plasticizing the resin, further accelerates residual stress relaxation. Crossman and Flaggs^[74, 101] compared results of a linear viscoelastic analysis of dimensional changes in laminates with experimental data and the results of elastic analysis. The correlation between viscoelastic analysis and experimental data (warping) was very good. The elastic model failed especially when used to analyze 121°C cure material (GY70/CE339). The viscoelastic model supported earlier observations (i.e. Crossman, Mauri and Warren^[69]) that the viscoelastic stress relaxation during complete moisture absorption-desorption cycle at constant temperature can lead to unrecoverable dimensional changes and result in different residual stress state. Thus accelerated conditioning programs may result in a changed residual stress state. Crossman et al^[69] found that hygrothermal cycling increased residual stresses in a T300/5209 unsymmetric laminate. Similar laminates made from T300/5208 showed a 5-10% loss of residual stress under the same thermal history.

Hedrick and Whiteside^[28] demonstrated that choosing an appropriate cooling rate for graphite/epoxy laminates (based on 3501 epoxy), may also reduce the residual stresses through relaxation. Stress relaxation was studied (Fig. 42) and different cooling rates from 177°C to 121°C were investigated. In Table 4, a summary of photomicrographic examinations is given.

Harper and Weitsman^[24] and Douglas and Weitsman^[94] postulated that if residual stress relaxation is possible, then there should be an optimum cool down path for a laminate. They used a linear viscoelastic model to find this path. Experimental confirmation of their finding has not been very successful so far, as specimens used were relatively thick and contained many transverse cracks which obscured the results (an AS-3502 system was used). Further experiments in this optimal time-temperature path are continuing.

6.3 Conclusions

- 1) The mismatch of thermal and moisture expansion of constituent materials or individual plies in a laminate is responsible for build up of residual stress states. Residual stresses are usually significant under normal usage conditions.
- 2) Residual stresses (or cure stresses) may cause transverse and interlaminar cracks in laminates before any external load has been applied. These stresses may be reduced by taking advantage of stress relaxation techniques.
- 3) Viscoelastic models seem to be better suited for studying residual stresses in composites.
- 4) When accelerated hygrothermal conditioning programs are used, care should be taken, as a residual stress state may result which would not be found under normal service conditions.

TABLE 1

GLASS TEMPERATURE^[283]

Sample	M _s g/100g	HDT(°C) Penetration	Tg(°C) Dilatometry
5209	Dry	134	154
	3.730	95	90
6-Ply	Dry	109	131
	1.236	90	109
12-Ply	Dry	116	131
	1.329	96	109

TABLE 2
SMOOTHED VALUES OF THE LINEAR THERMAL EXPANSION COEFFICIENT α OF THE SPECIMENS
AT THREE REPRESENTATIVE TEMPERATURES(229)

Fibre Lay-Up*	Fibre Volume Fraction (%)	Area of Plate Containing More Than 1% Voids (%)	Area of Plate Containing More Than 2% Voids (%)	$\alpha(^{\circ}\text{C}^{-1})$ at -150°C	$\alpha(^{\circ}\text{C}^{-1})$ at 0°C	$\alpha(^{\circ}\text{C}^{-1})$ at 150°C
100%/0°	67.1	0	0	-0.81×10^{-7}	-1.69×10^{-7}	-1.47×10^{-7}
75%/0°, 25%/±45°	65.8	0	0	-2.95×10^{-7}	-4.29×10^{-7}	-0.27×10^{-7}
50%/0°, 50%/±45°	68.6	5	0	1.40×10^{-7}	0.22×10^{-7}	4.72×10^{-7}
25%/0°, 75%/±45°	69.3	5	0	6.90×10^{-7}	7.85×10^{-7}	1.22×10^{-6}
50%/0°, 50%/90°	65.1	0	0	1.75×10^{-6}	1.88×10^{-6}	2.96×10^{-6}
25%/90°, 75%/±45°	69.3	5	0	3.65×10^{-6}	4.38×10^{-6}	5.15×10^{-6}
50%/90°, 50%/±45°	68.6	5	0	5.94×10^{-6}	7.98×10^{-6}	1.10×10^{-5}
75%/90°, 25%/±45°	65.8	0	0	8.55×10^{-6}	1.26×10^{-5}	1.75×10^{-5}
100%/90°	67.1	0	0	1.56×10^{-5}	2.41×10^{-5}	3.03×10^{-5}
No fibers				2.68×10^{-5}	4.45×10^{-5}	6.76×10^{-5}

* In relation to the direction of measurement

TABLE 3
THERMAL CYCLING EFFECTS ON LONGITUDINAL CTE⁽⁴⁶⁾

Material System	Fiber Volume, %	Longitudinal CTE, $\mu\text{in./in.}^\circ\text{F}$	
		As-Cured	Thermally Cycled
HMS/934, U/D	65.6	-0.45	-0.35
HMS/3501, U/D	65.2	-0.35	-0.38
HMS/934, O/D	65.1	-0.10	-0.30
HMS/3501, O/D	69.5	-0.13	-0.26
HMS/339, O/D	60.6	-0.10	-0.12
Hybrid (HMS/3501 + T-300/934)	63.3	-0.13	-0.25

Note: U/D = unidirectional; O/D = oriented.

TABLE 4
SUMMARY OF PHOTOMICROGRAPHIC EXAMINATION OF Gr/Ep LAMINATES⁽¹²⁸⁾

Cooling Rate (350°F to 250°F), °F/min.	No. Specimens Examined	Total Area* Examined, in. ²	Total No. of Cracks	Max. Crack Length, in.
5 to 6	3	3.24	47	0.012
2.5	2	1.89	3	0.005
1	9	7.21	0	—

* Microscopic examination of sectioned sine wave spars and travelers (300 X to 500 X)

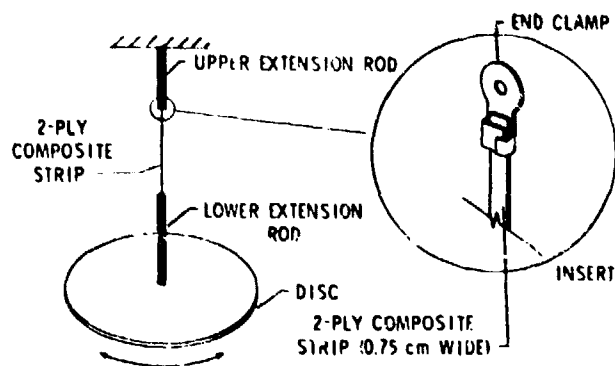


FIG. 1: SKETCH OF THE TBA PENDULUM. INSERT SHOWS METHOD USED TO ATTACH END CLAMPS TO COMPOSITE SPECIMEN[281]

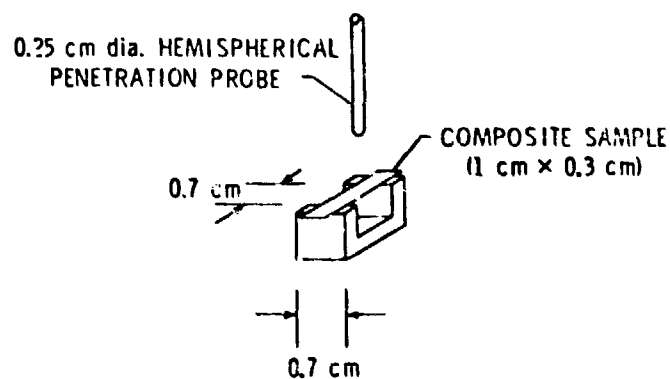


FIG. 2: SCHEMATIC OF THE TMA SAMPLE SUPPORT FIXTURE USED TO DETERMINE HEAT DISTORTION TEMPERATURES IN COMPOSITE MATERIALS[281]

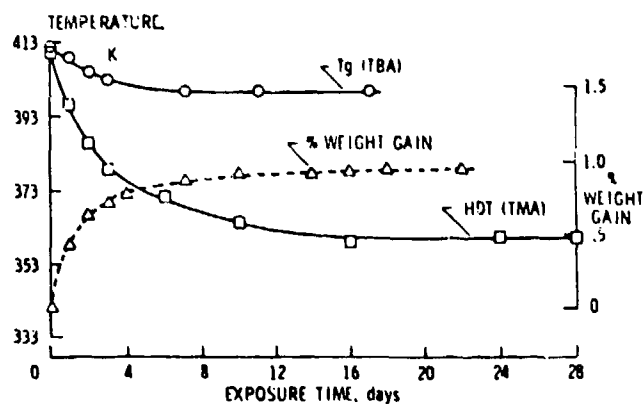


FIG. 3: EFFECT OF SOAK TIME ON THE HDT, T_g AND MOISTURE PICK UP OF A 2-PLY UNIDIRECTIONAL T-300/5209 COMPOSITE CURED AT 400 K[281]

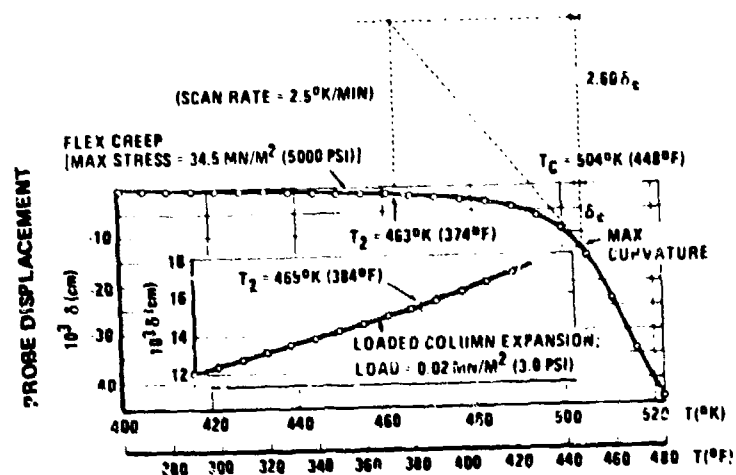


FIG. 4: TMA FLEXURE AND COLUMN LOADING RESULTS FOR DRY 5208 RESIN[52]

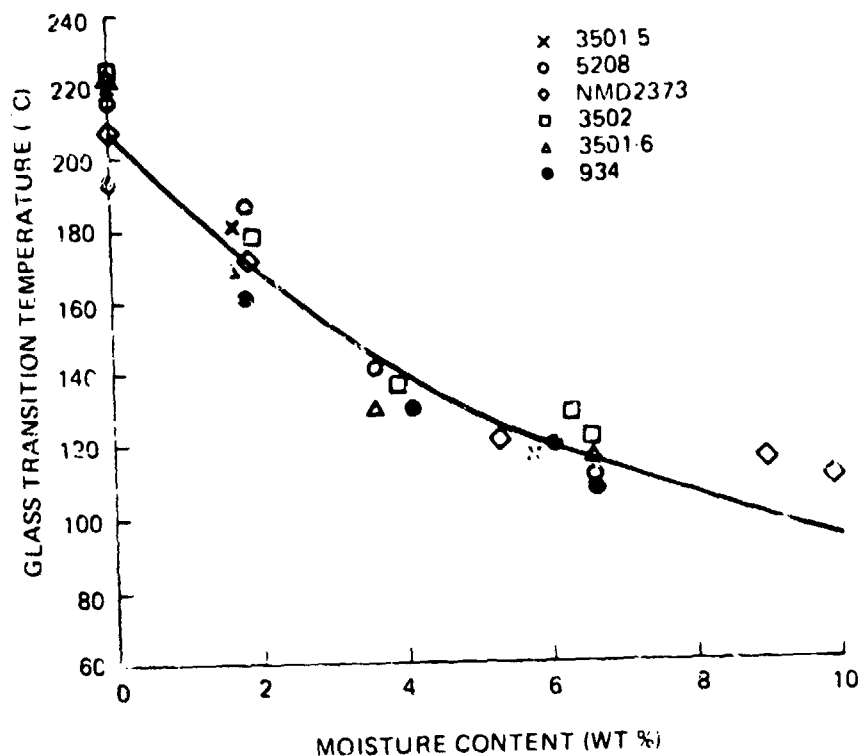


FIG. 5: RELATIONSHIP BETWEEN EQUILIBRIUM MOISTURE CONCENTRATION AND GLASS TRANSITION TEMPERATURE OF EPOXY RESINS[81]

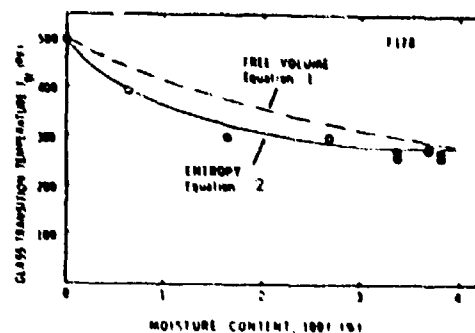


FIG. 6: VARIATION OF GLASS TRANSITION TEMPERATURE WITH MOISTURE CONTENT FOR CURED F178 POLYIMIDE RESIN. SOLID CURVE IS PREDICTION OF ENTROPY MODEL, EQUATION 2, USING $T_{g0} = 533^{\circ}\text{K}$ AND ARBITRARY PARAMETERS $M_s = 270 \text{ g/mole}$, $\Delta C_p = 0.022 \text{ cal/g}^{\circ}\text{C}$. DASHED CURVE IS PREDICTION OF FREE VOLUME THEORY, EQUATION 1, WITH $T_{gp} = 533^{\circ}\text{K}$, $\alpha_p = 1.98 \times 10^{-4}^{\circ}\text{C}^{-1}$, $T_{gd} = 4^{\circ}\text{C}$, $\alpha_d = 3.66 \times 10^{-3}^{\circ}\text{C}^{-1}$ [51]

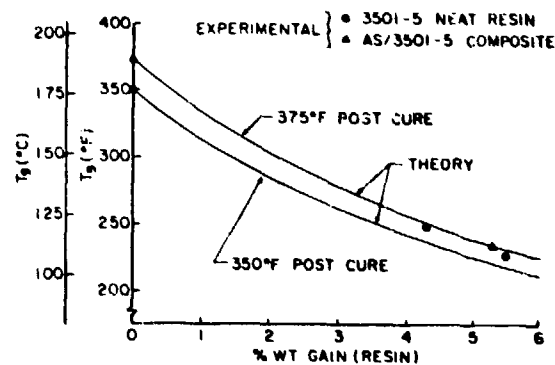


FIG. 7: GLASS TRANSITION TEMPERATURE AS A FUNCTION OF ABSORBED MOISTURE IN RESIN [41]

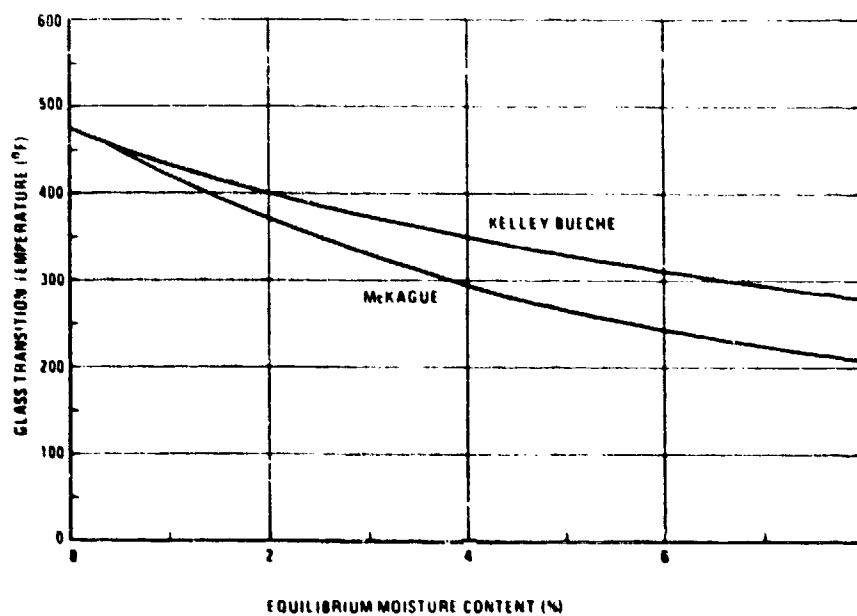


FIG. 8: COMPARISON OF GLASS TRANSITION MODELS^[214]

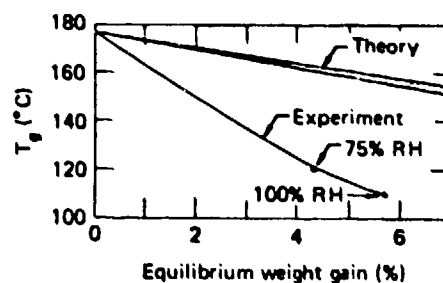


FIG. 9: THEORETICAL AND EXPERIMENTAL VALUES OF T_g AS A FUNCTION OF EQUILIBRIUM MOISTURE WEIGHT GAIN FOR A TGDDM-DDS EPOXY-MOISTURE SYSTEM^[220]

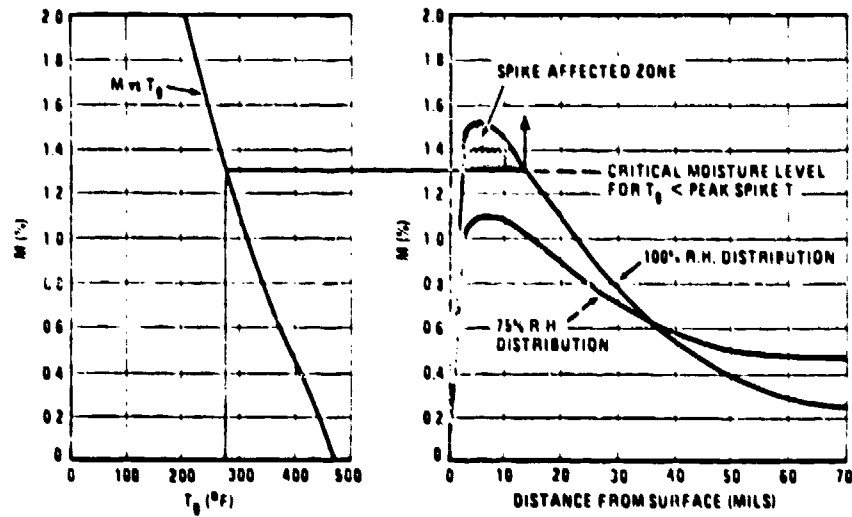


FIG. 10: RELATIONSHIP OF T_g , PEAK SPIKE TEMPERATURE AND MOISTURE DISTRIBUTION TO THE THERMAL SPIKE EFFECT [211]

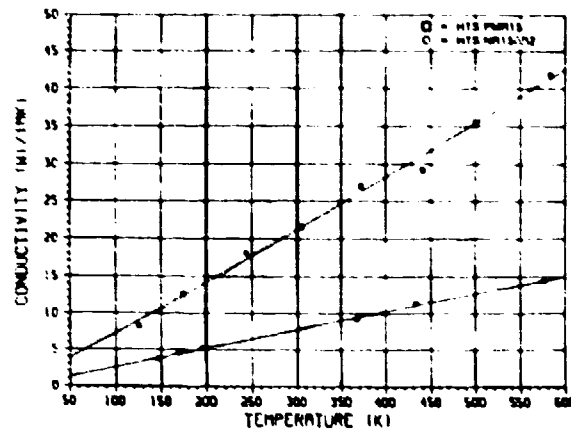


FIG. 11: THERMAL CONDUCTIVITY, $[0^{\circ}]_n$ COMPARISON (CUT BAR) [48]

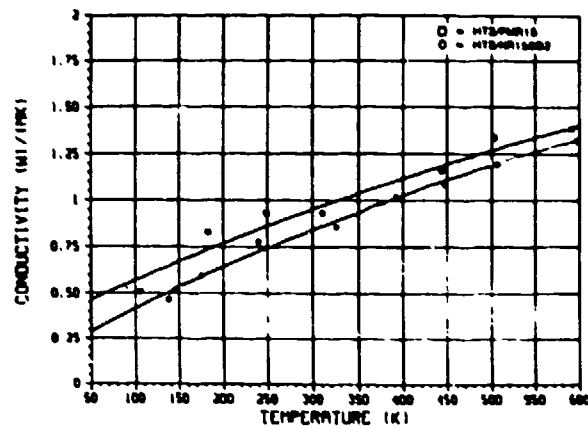


FIG. 12: THERMAL CONDUCTIVITY, $[90^{\circ}]_n$ COMPARISON (HOT PLATE) [48]

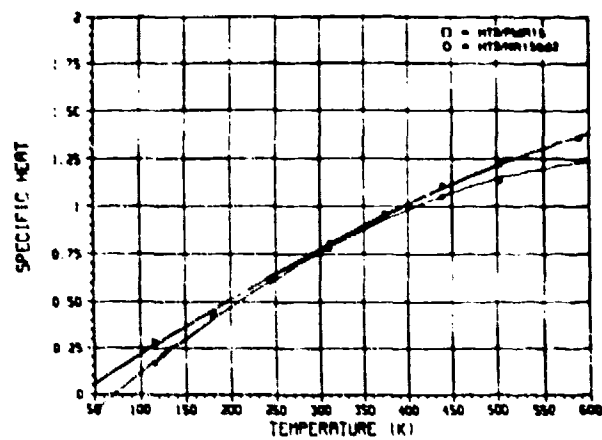


FIG. 13: SPECIFIC HEAT COMPARISON ISOTROPIC LAY-UP[48]

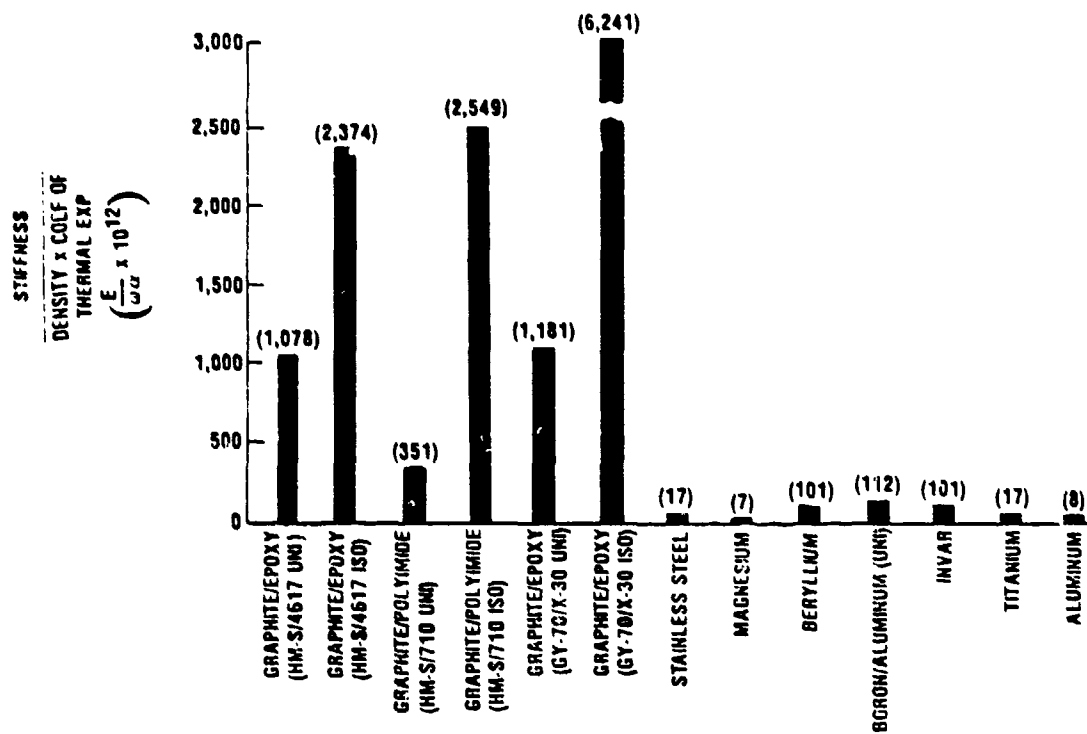
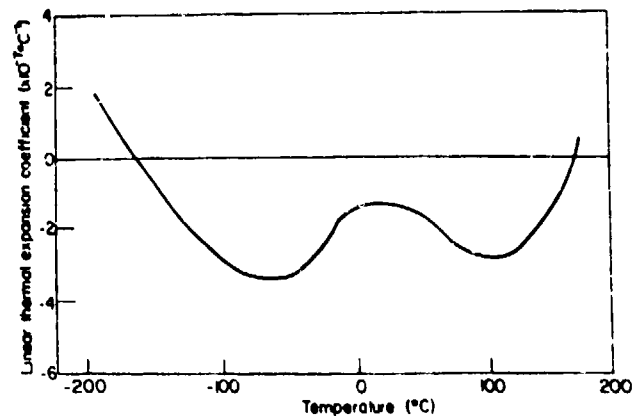
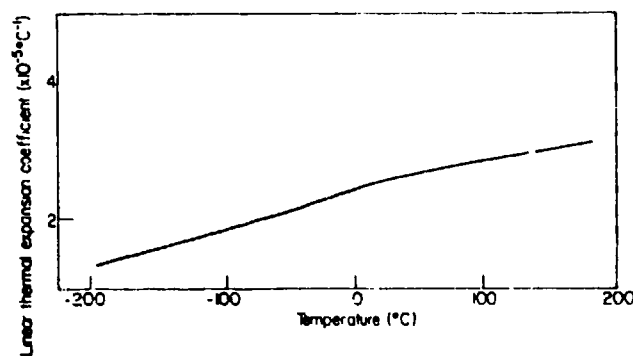


FIG. 14: RELATIVE MERITS OF CANDIDATE MATERIALS[130]

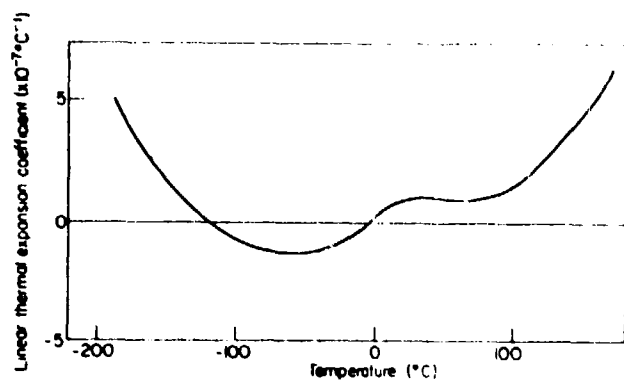


(a)

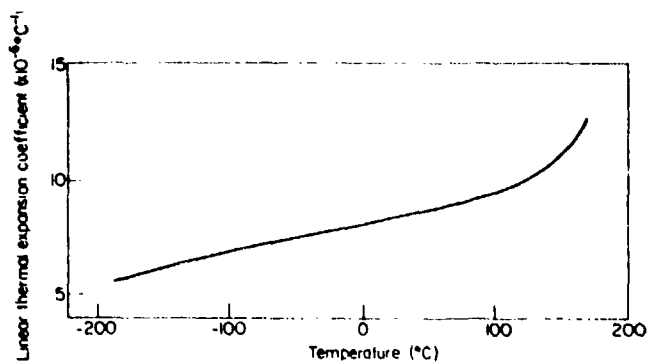


(b)

FIG. 15: THE LINEAR THERMAL EXPANSION COEFFICIENT OF $[0^\circ]_{16}$ LAMINATE IN (a) LONGITUDINAL AND (b) TRANSVERSE DIRECTION[229]



(a)



(b)

FIG. 16: THE LINEAR THERMAL EXPANSION OF $[+45^{\circ}, 0^{\circ}, -45^{\circ}, 0^{\circ}]_2$ LAMINATE IN (a) LONGITUDINAL AND (b) TRANSVERSE DIRECTION[229]

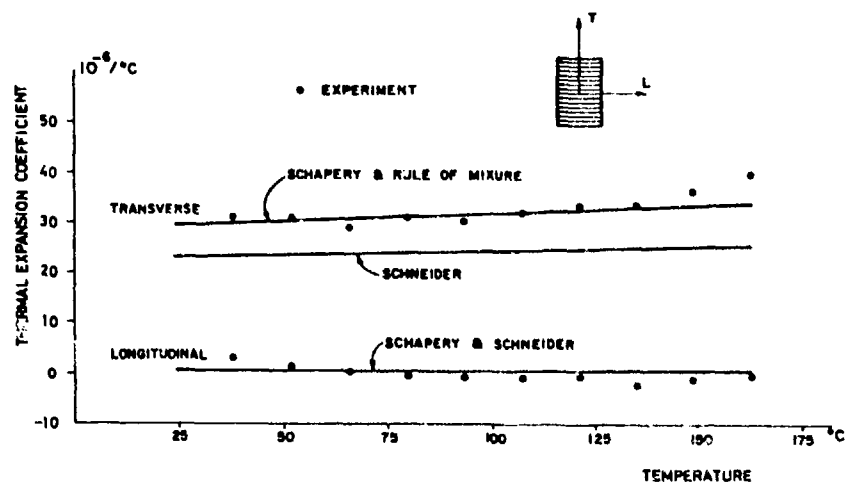


FIG. 17: COMPARISON OF THE CTE BETWEEN EXPERIMENT AND THEORY[303]

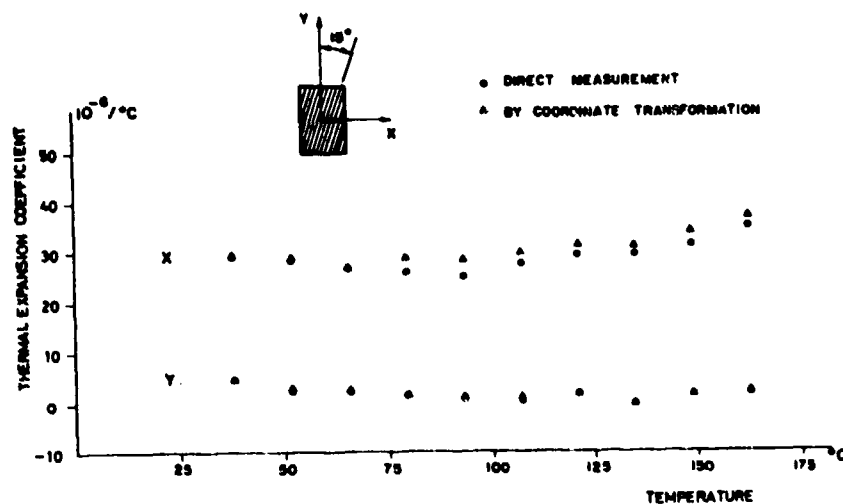


FIG. 18: COMPARISON OF THE CTE BETWEEN DIRECT MEASUREMENT AND COORDINATE TRANSFORMATION[303]

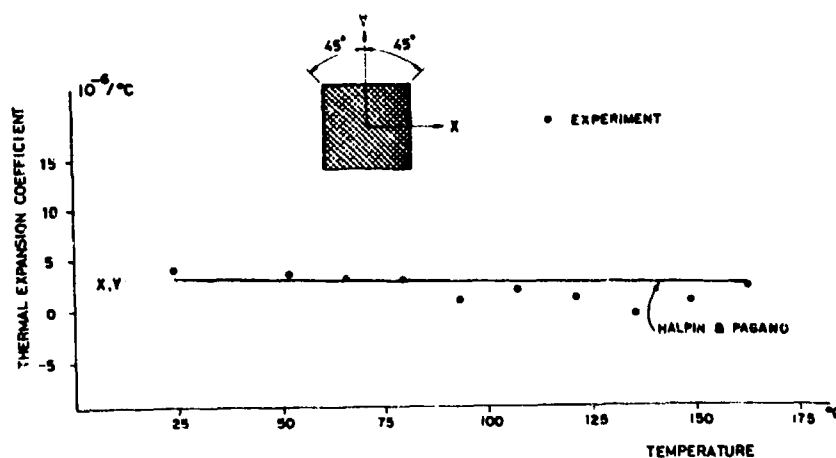
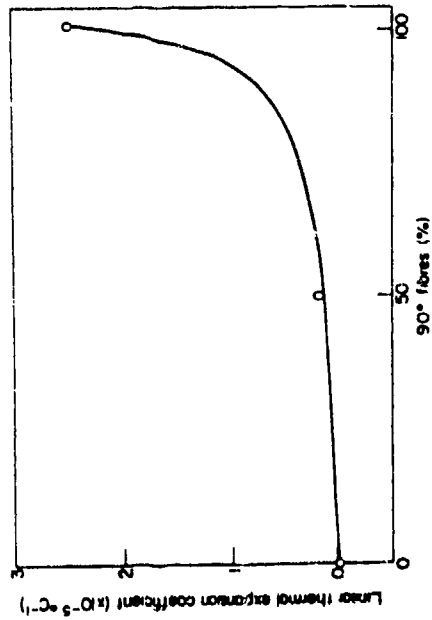
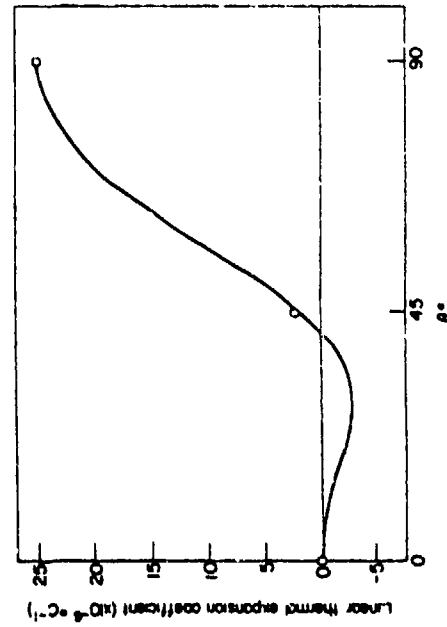


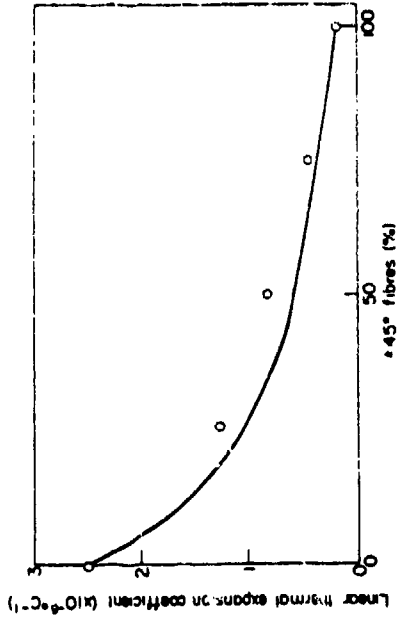
FIG. 19: COMPARISON OF THE CTE FOR A ± 45 -DEG LAMINATE BETWEEN EXPERIMENT AND THEORY[303]



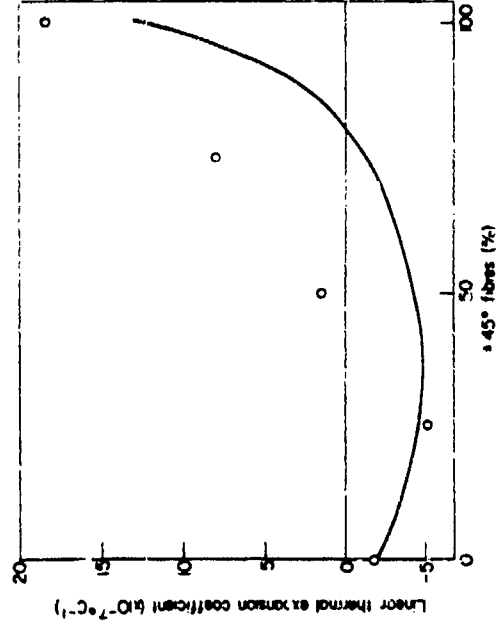
The room temperature linear thermal expansion coefficient of 0° , 90° laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated



The room temperature linear thermal expansion coefficient of symmetrically balanced angle-ply ($\pm \theta$) laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated



The room temperature linear thermal expansion coefficient of 90° , $\pm 45^\circ$ laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated



The room temperature linear thermal expansion coefficient of 0° , $\pm 45^\circ$ laminates consisting of Fibredux 914C resin containing Courtaulds HTS carbon fibre present at 66% by volume: o — experimental; solid line — calculated

FIG. 20: THE ROOM TEMPERATURE LINEAR CTE'S [229]

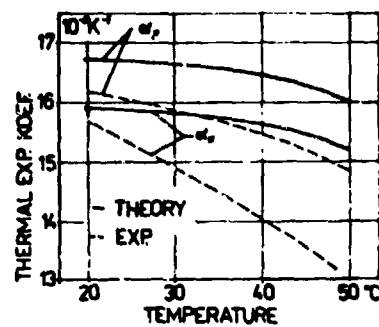


FIG. 21: COMPARISON OF THE THEORETICAL AND EXPERIMENTAL RESULTS^[150]

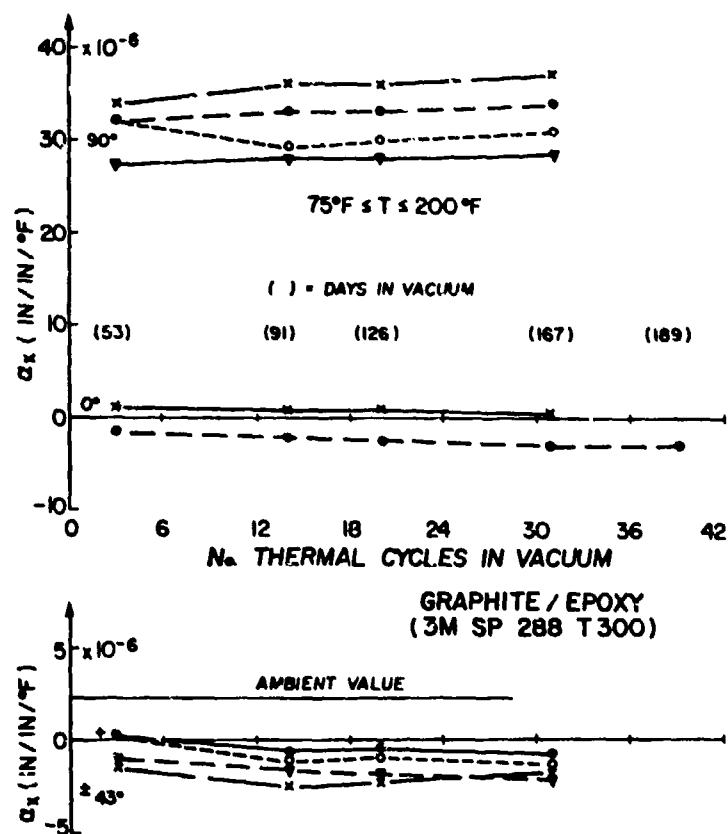


FIG. 22: THE EFFECT OF THERMAL CYCLING IN VACUUM ON CTE OF GRAPHITE/EPOXY^[286]

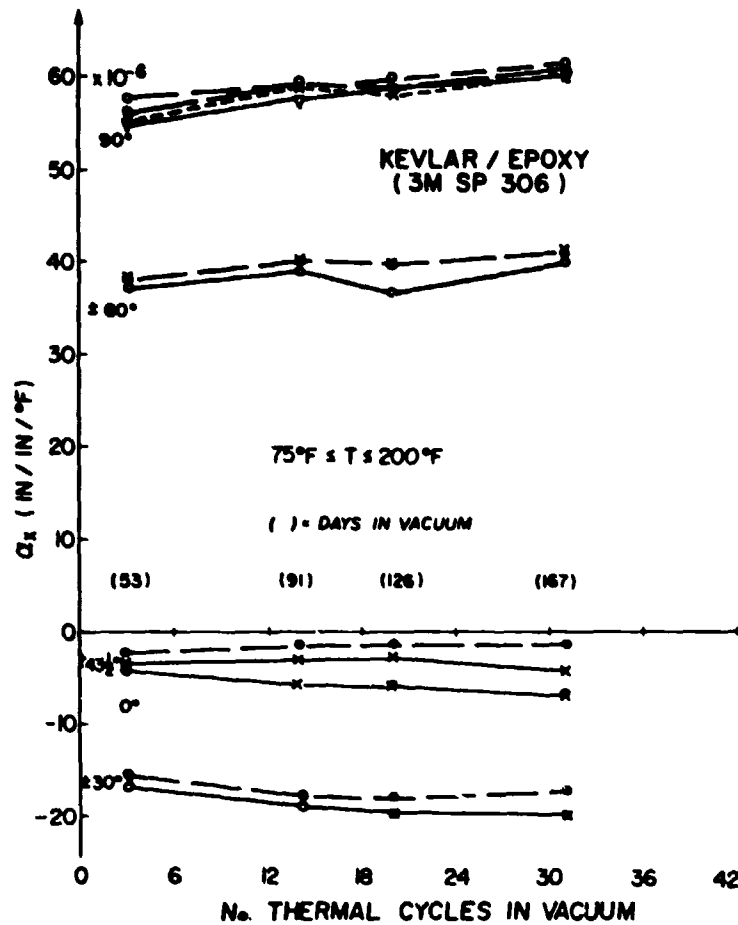


FIG. 23: THE EFFECT OF THERMAL CYCLING IN VACUUM ON CTE OF KEVLAR/EPOXY⁽²⁸⁶⁾

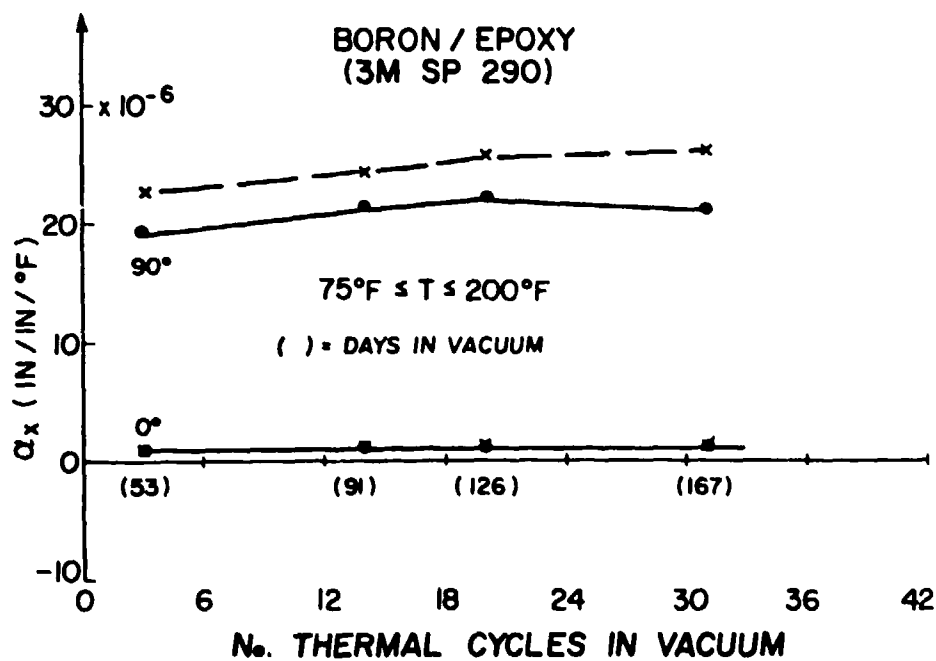


FIG. 24: THE EFFECT OF THERMAL CYCLING IN VACUUM ON BORON/EPOXY⁽²⁸⁶⁾

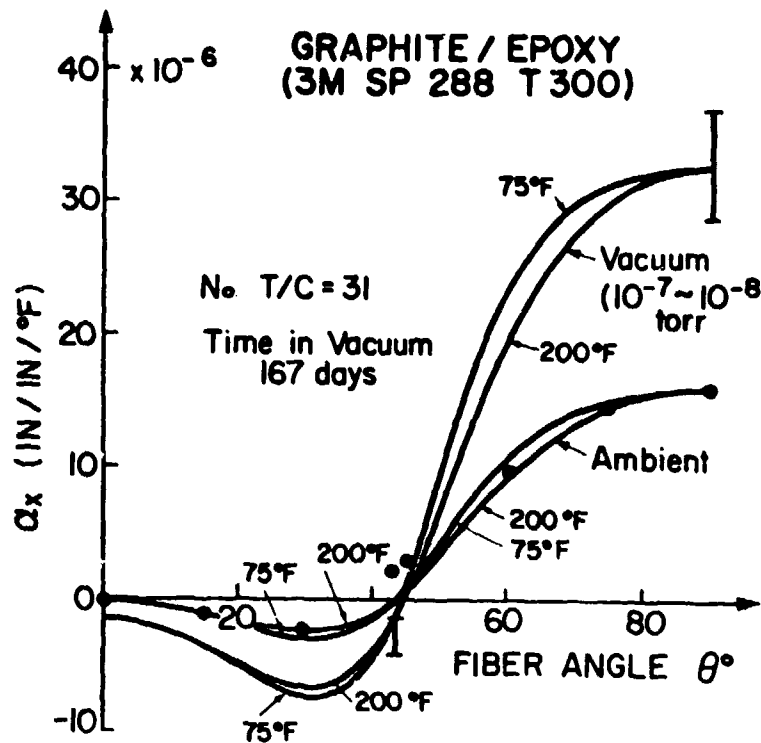


FIG. 25: COMPARISON OF CTE PREDICTED FOR VARIOUS θ WITH THE DATA^[286]

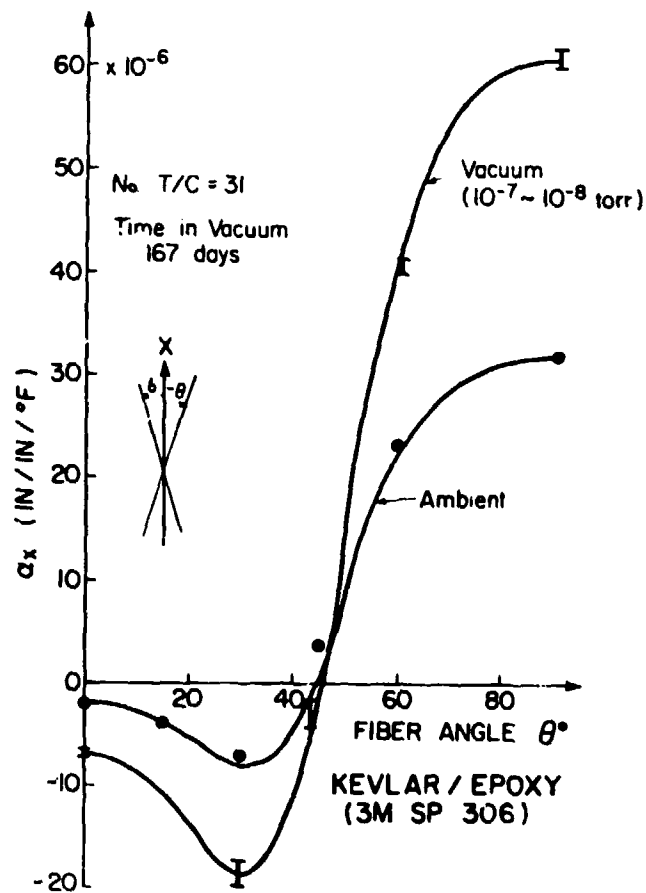


FIG. 26: COMPARISON OF CTE PREDICTED FOR VARIOUS θ WITH THE DATA^[286]

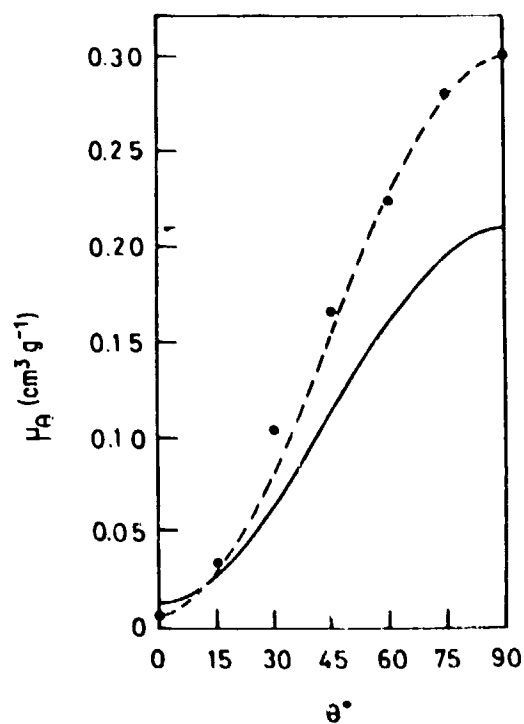


FIG. 27: COEFFICIENTS OF HYGROELASTICITY AS FUNCTIONS OF θ , COMPARED WITH THE CALCULATION BASED ON EXPERIMENTAL μ_L AND μ_T (---), AND ON μ_L AND μ_T WORKED OUT BY SCHAPERY'S EQUATIONS TAKING THE CONSTITUENTS' ORIGINAL PROPERTIES (—). [206]

● MEASURED

$$\mu = \frac{\Delta L/L_o}{\Delta \omega V_o}$$

L_o = length of specimen

$\Delta \omega$ = weight of water absorbed

V_o = original volume

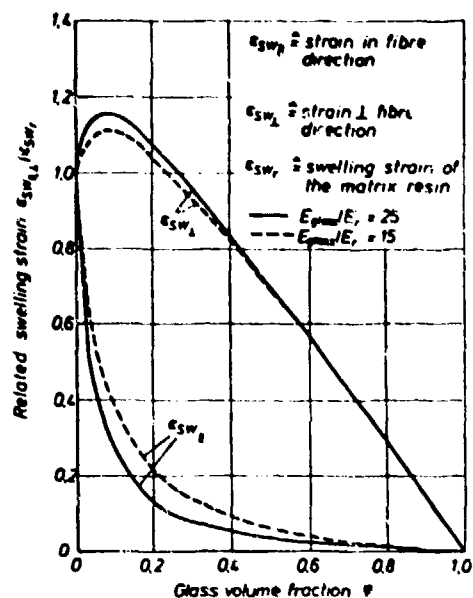


FIG. 28: SWELLING STRAIN BEHAVIOR OF ANISOTROPICALLY REINFORCED INDIVIDUAL LAYERS DUE TO MATRIX SWELLING^[216]

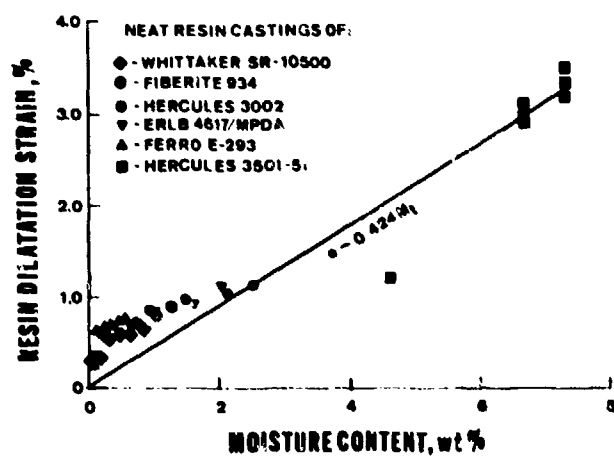


FIG. 29: SWELLING BEHAVIOR IS SIMILAR FOR SEVERAL EPOXIES^[262]

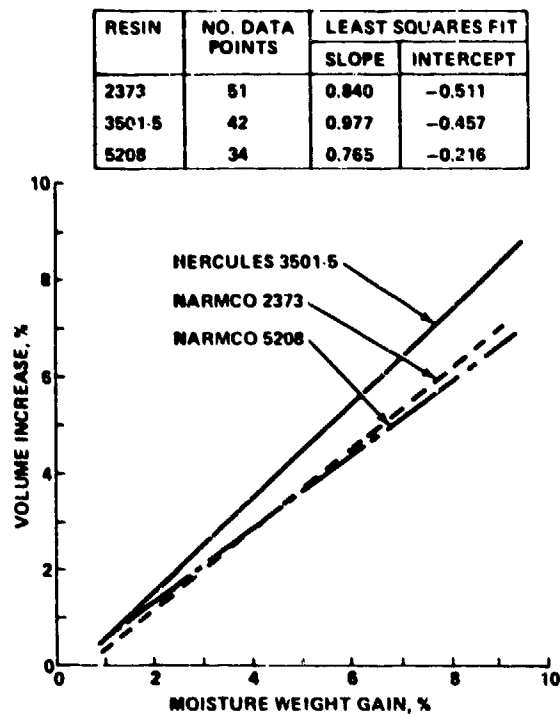


FIG. 30: RESIN SWELLING DUE TO ABSORBED MOISTURE^[128]

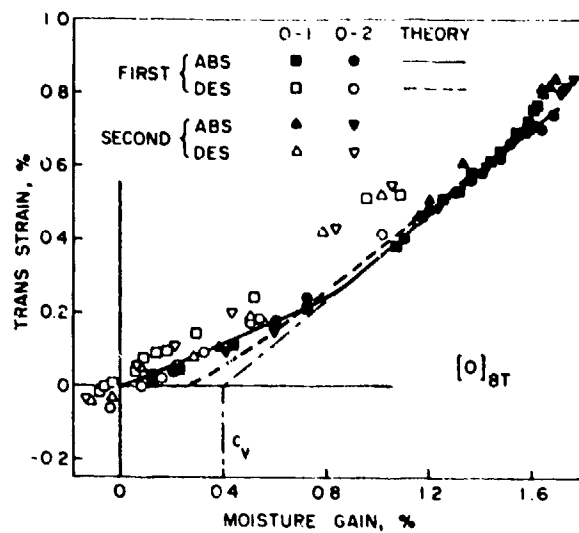


FIG. 31: TRANSVERSE SWELLING STRAIN OF $[0]_{BT}$ LAMINATE (AS/3501-5)^[118]

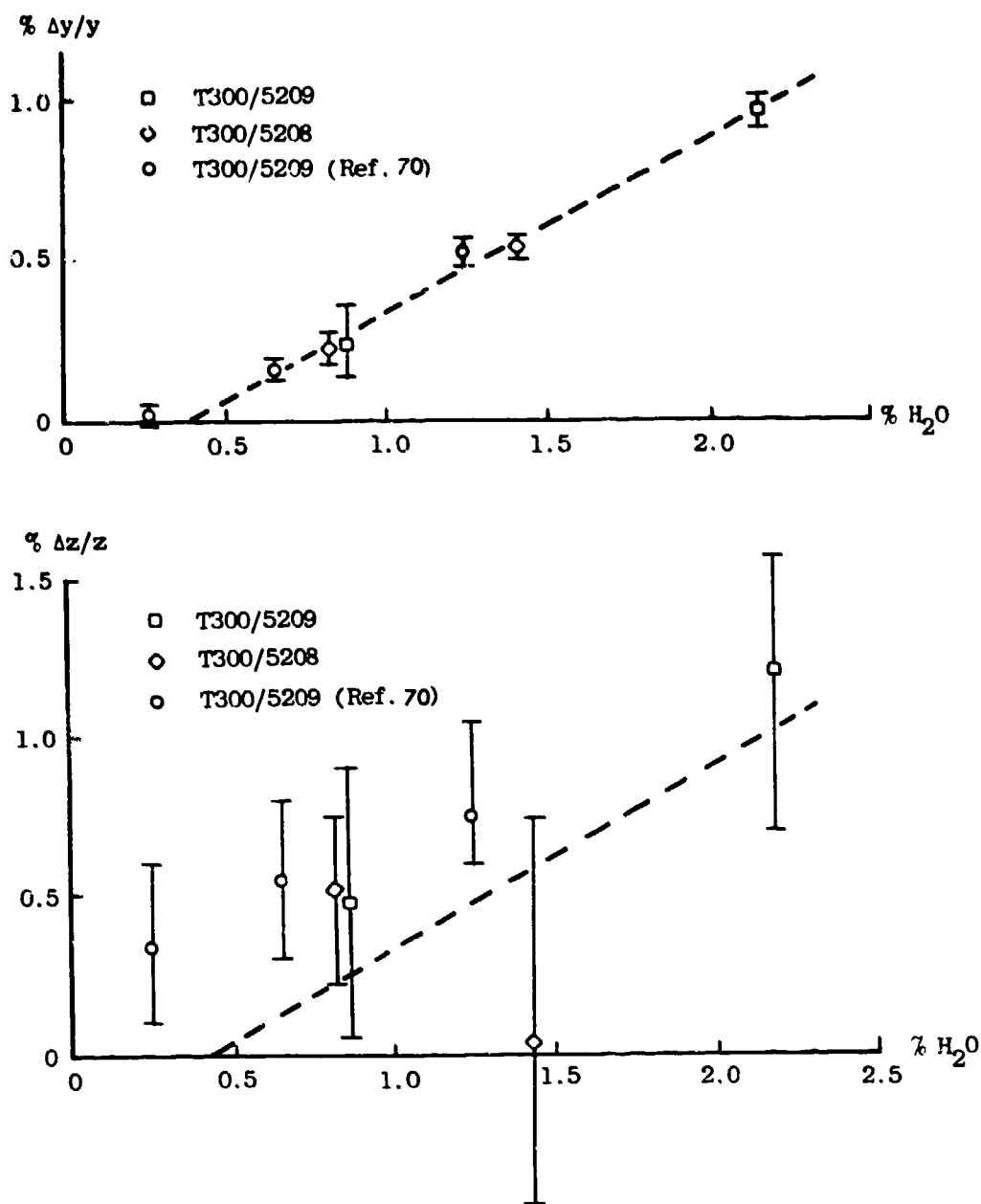


FIG. 32: DIMENSIONAL CHANGES IN TRANSVERSE ($\Delta y/y$) AND THROUGH THICKNESS ($\Delta z/z$) DIRECTIONS IN UNIDIRECTIONAL COMPOSITES vs EQUILIBRIUM MOISTURE CONTENT^[69]

The dotted line represents linear regression on $\Delta y/y$ data for both graphs ($\Delta z/z$ seems to be greater than $\Delta y/y$)

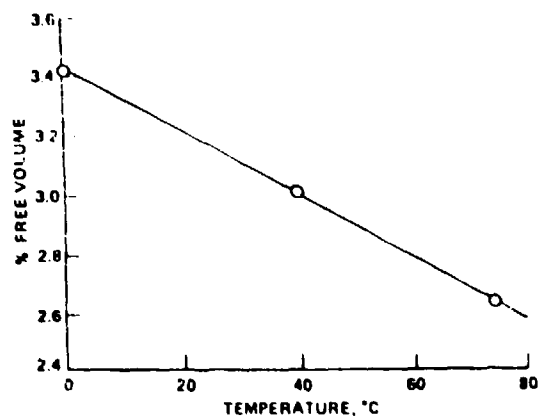


FIG. 33: PERCENT FREE VOLUME AS A FUNCTION OF TEMPERATURE, HERCULES 3501 RESIN. VALUES OF 74 AND 40°C DETERMINED BY SWELLING DATA DURING ABSORPTION. VALUE AT 1°C DETERMINED USING REVERSE THERMAL EFFECT FROM 74°C EQUILIBRIUM[4]

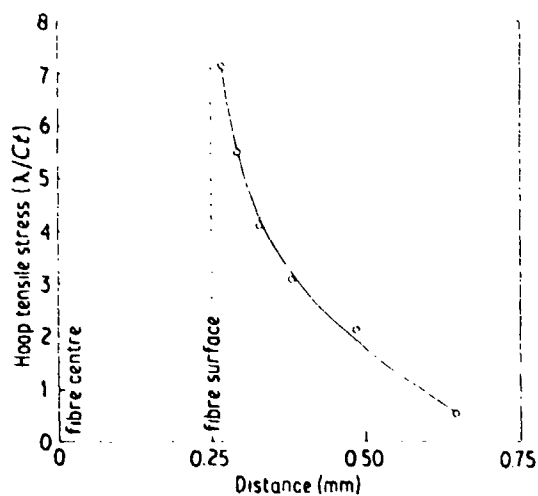


FIG. 34: PLOT OF THE HOOP TENSILE STRESS AGAINST RADIAL DISTANCE FROM THE FIBRE[75]

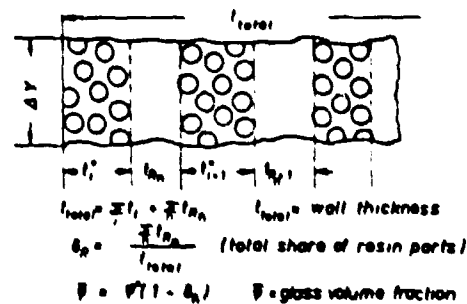


Fig. 1 Inhomogeneous fiber distribution in a (statistically) representative volume element

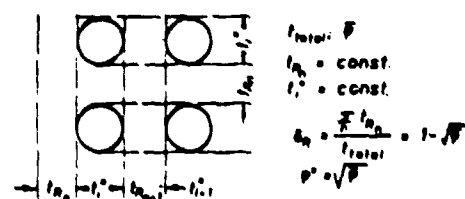


Fig. 2 Layer with homogeneous fiber distribution

FIG. 35: SCHEMATICAL REPRESENTATION OF RESIN AND FIBRE DISTRIBUTION[216]

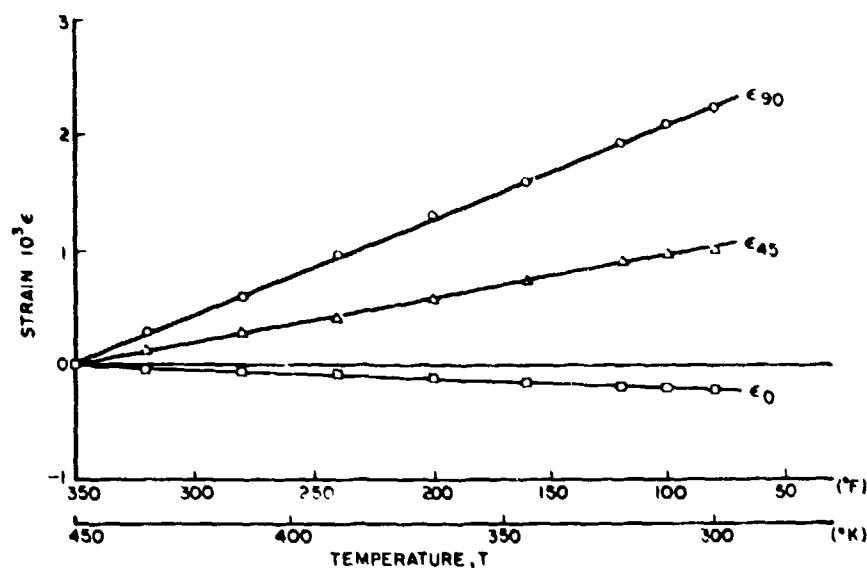


FIG. 36: RESIDUAL STRAINS IN 0-DEG PLIES OF $[0_2/\pm 45]_s$ BORON-EPOXY SPECIMEN[78]

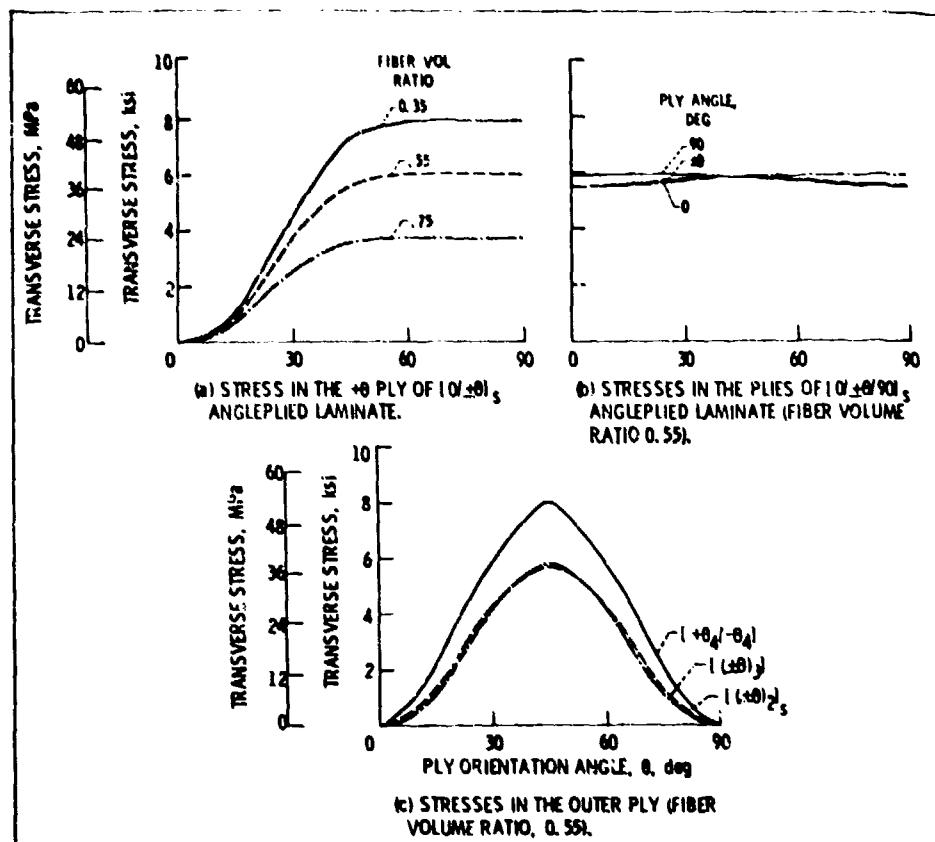


FIG. 37: PLY RESIDUAL TRANSVERSE STRESS FOR GRAPHITE THORNEL-50/EPOXY COMPOSITES. TEMPERATURE DIFFERENCE, 167 K (300°F) (53)

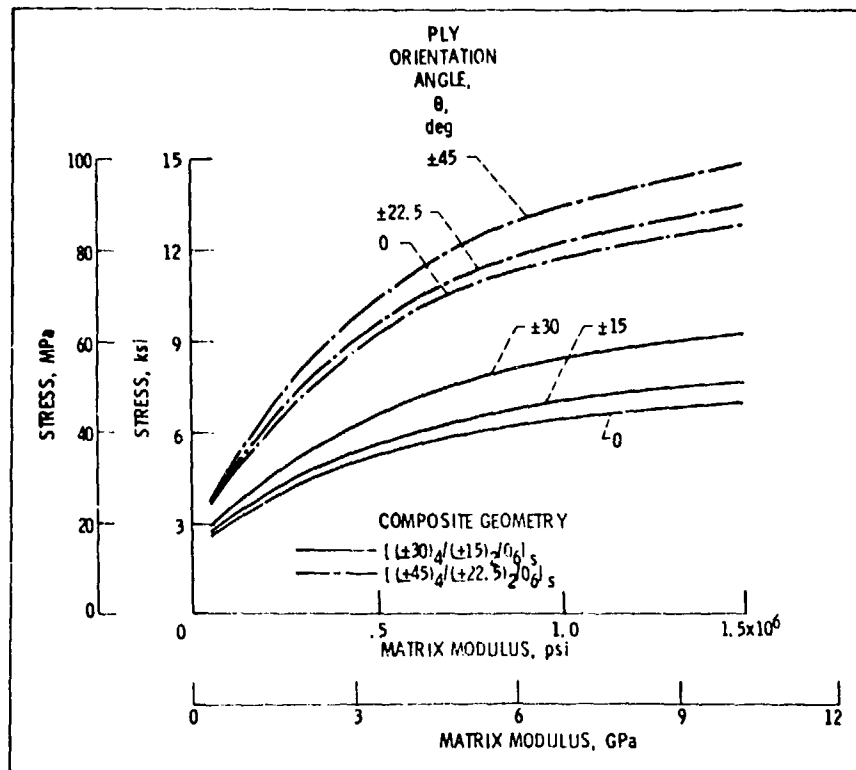


FIG. 38: EFFECT OF MATRIX MODULUS ON PLY RESIDUAL TRANSVERSE STRESS. MODMOR-I/ POLYIMIDE COMPOSITES; ZERO VOID CONTENT FIBER VOLUME RATIO, 0.50; TEMPERATURE DIFFERENCE, 333 K (600°F) [53]

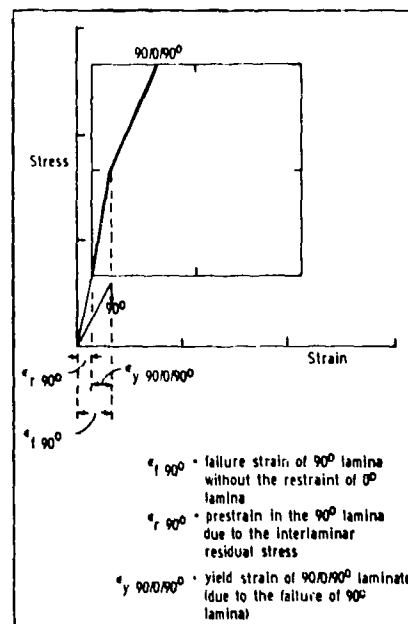


FIG. 39: APPROXIMATE RELATIONSHIP BETWEEN THE YIELD STRAIN OF A 90°/90° LAMINATE AND THE FAILURE STRAIN OF A 90° LAMINA (WITHOUT THE RESTRAINT OF A 0° LAMINA) [188]

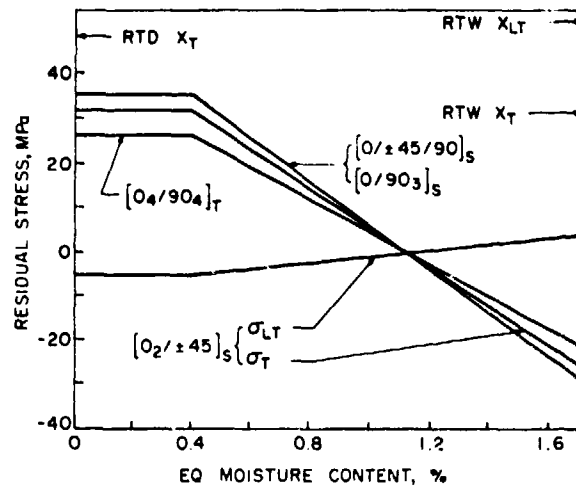


FIG. 40: RESIDUAL STRESSES VERSUS EQUILIBRIUM MOISTURE CONTENT FOR VARIOUS LAMINATES[118]

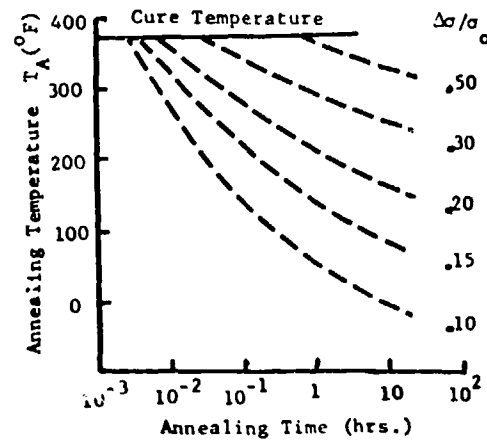


FIG. 41: KINETICS OF 1031 STRESS RELAXATION AS A FUNCTION OF ANNEALING TIME AND TEMPERATURE[73]

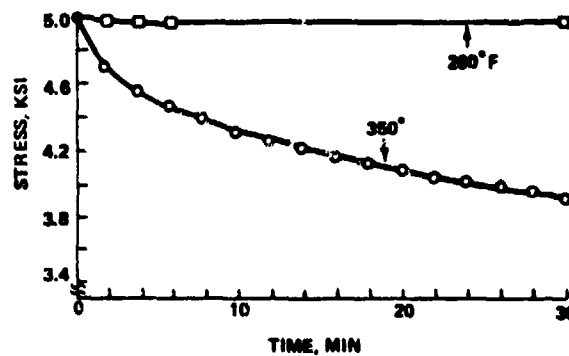


FIG. 42: STRESS RELAXATION OF HERCULES 3601-5A RESIN[128]

APPENDIX A - BIBLIOGRAPHY

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REPORT DOCUMENTATION PAGE / PAGE DE DOCUMENTATION DE RAPPORT

REPORT/RAPPORT NAE-AN-10 1a		REPORT/RAPPORT NRC No. 22700 1b		
REPORT SECURITY CLASSIFICATION CLASSIFICATION DE SÉCURITÉ DE RAPPORT 2 Unclassified		DISTRIBUTION (LIMITATIONS) 3 Unlimited		
TITLE/SUBTITLE/TITRE/SOUS-TITRE Hygrothermal Effects in Continuous Fibre Reinforced Composites Part II: Physical Properties 4				
AUTHOR(S)/AUTEUR(S) J.P. Komorowski 5				
SERIES/SÉRIE Aeronautical Note 6				
CORPORATE AUTHOR/PERFORMING AGENCY/AUTEUR D'ENTREPRISE/AGENCE D'EXÉCUTION National Research Council Canada National Aeronautical Establishment Structures and Materials Laboratory 7				
SPONSORING AGENCY/AGENCE DE SUBVENTION 8				
DATE 83-09 9	FILE/DOSSIER 10	LAB. ORDER COMMANDE DU LAB. 11	PAGES 62 12a	FIGS/DIAGRAMMES 42 12b
NOTES 13				
DESCRIPTORS (KEY WORDS)/MOTS-CLÉS 1. Carbon fibre reinforced plastics 2. Composite materials 14				
SUMMARY/SOMMAIRE <p>This report is second in a series of literature reviews in which hygrothermal effects on aerospace composite materials (CM) with polymeric matrixes are examined. This report (Part II) deals primarily with the glass transition temperature and expansion properties due to temperature and moisture. The chapter on residual stresses is also included in this part as these stresses are a direct consequence of the expansion properties. Specific heat, thermal conductivity and emittance are briefly mentioned in Chapter 3.0, while properties connected with moisture absorption have been reviewed extensively in Part I of the series.</p> <p>Other reports in this series deal with the following topics:</p> <p>Part I: Thermal and Moisture Diffusion Part III: Mechanical Properties 1 Part IV: Mechanical Properties 2 Part V: Composite Structures and Joints Part VI: Numerical and Analytical Solutions Part VII: Summary of Conclusions and Recommendations</p> 15				